Interpocket polarization model for magnetic structures in rare-earth hexaborides

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The origin of peculiar magnetic structures in cubic rare-earth (R) hexaborides RB_6 is traced back to their characteristic band structure. The three sphere-like Fermi surfaces induce interpocket polarization of the conduction band as a part of a RKKY-type interaction. It is shown for the free-electron-like model that the interpocket polarization gives rise to a broad maximum in the intersite interaction $I(\boldsymbol{q})$ around $\boldsymbol{q} = (1/4, 1/4, 1/2)$ in the Brillouin zone. This maximum is consistent with the superstructure observed in R=Ce, Gd and Dy. The wave-number dependence of $I(\boldsymbol{q})$ is independently extracted from analysis of the spin-wave spectrum measured for NdB_6. It is found that $I(\boldsymbol{q})$ obtained from fitting the data has a similarly to that derived by the interpocket polarization model, except that the absolute maximum now occurs at $(0, 0, 1/2)$ in consistency with the A-type structure. The overall shape of $I(\boldsymbol{q})$ gives a hint toward understanding an incommensurate structure in PrB_6 as well.

KEYWORDS: GdB_6, NdB_6, PrB_6, CeB_6, hexaborides, RKKY interaction, elastic constant, quadrupolar interaction

Interest in cubic rare-earth (R) hexaborides RB_6 comes mainly from the rich structure in their ordered phases. The best studied example is CeB_6 which undergoes a quadrupole (orbital) order at 3.3 K and then a magnetic order at 2.4 K.[1] The magnetic ground state is characterized by double-$\boldsymbol{k}$ structure with wave vectors $(1/4, \pm 1/4, 1/2)$ in units of the reciprocal lattice parameter $2\pi/a$. Since the orbital order is superimposed on the magnetic order, it has been suspected that the orbital degeneracy in the crystalline electric field (CEF) ground state Γ_8 plays an important role.[2] Recently, however, neutron scattering experiment on GdB_6 has detected an equivalent wave vector in the ordered phase below 15 K.[3] Since the trivalent Gd ion has a half-filled 4f shell without orbital degrees of freedom, the order at $\boldsymbol{k} = (1/4, 1/4, 1/2)$ should have an origin which does not depend so much on the particular configuration of 4f electrons. It is known that PrB_6 also has the same wave number in the magnetically ordered ground state below 4.2 K, but the intermediate phase between 4.2 K and 6.9 K has an incommensurate structure.[4] On the other hand, the ground state of NdB_6 has a simple antiferromagnetic structure called the type I (or A-type) with alternating plane polarized along and against (0,0,1).[5,6]

In this paper we propose a simple model to understand the origin of these structures from a unified point of view. The basic observation is that the Fermi surface of RB_6 consists of three nearly spherical pieces centered on the X points $X_x = (1/2, 0, 0), X_y = (0, 1/2, 0), X_z = (0, 0, 1/2)$ in the Brillouin zone. The RKKY interaction involves interpocket polarization, which has a new characteristic wave vector $\boldsymbol{K}_3 = (1/2, 1/2, 0)$ which connects X_x and X_y, and equivalent ones. Just like the ordinary RKKY interaction can bring about the antiferromagnetic ordering by halving the reciprocal lattice vector, the halving of the characteristic wave vector $(1/2, 1/2, 0)$ can bring about the ordering at $(1/4, 1/4, 1/2)$.

Let us consider the case of GdB_6 where the 4f electrons have only the spin degrees of freedom. The exchange interaction between a 4f-spin $\boldsymbol{S}_i$ at $\boldsymbol{R}_i$ and conduction electrons is taken to be

$$H_{df} = \frac{J}{N} \sum_{\boldsymbol{k},\boldsymbol{p}} \sum_i W_{\boldsymbol{k},\boldsymbol{p}} \mathrm{e}^{i(\boldsymbol{p}-\boldsymbol{k})\cdot\boldsymbol{R}_i} \boldsymbol{S}_i \cdot \boldsymbol{\sigma}_{\alpha\beta} c^\dagger_{\boldsymbol{k}\alpha} c_{\boldsymbol{p}\beta}, \quad (1)$$

where N is the number of lattice sites, and $JW_{\boldsymbol{k},\boldsymbol{p}}$ is determined by the exchange integral involving 4f wave functions and the conduction states. We follow the previous argument[7] to derive $JW_{\boldsymbol{k},\boldsymbol{p}}$. In analogy with the APW method we consider a muffin-tin sphere centered at the origin. The Bloch function $\psi_{\boldsymbol{k}}(\boldsymbol{r})$ of the conduction band is expanded inside the sphere as

$$\psi_{\boldsymbol{k}}(\boldsymbol{r}) = \frac{1}{\sqrt{N}} \sum_\lambda R_{k\lambda}(r) \sum_{\Gamma\gamma} d^{(\lambda)}_{\Gamma\gamma}(\boldsymbol{k}) Y^{(\lambda)}_{\Gamma\gamma}(\hat{r}), \quad (2)$$

where $R_{k\lambda}(r)$ describes the radial part with orbital index λ, and $Y^{(\lambda)}_{\Gamma\gamma}(\hat{r})$ with $\hat{r} = \boldsymbol{r}/r$ is the cubic harmonics for the point-group representation Γ and its component γ. We neglect the k-dependence of $R_{k\lambda}(r)$ since the extent of 4f electrons is smaller than that of 5d electrons which contribute dominantly to the exchange. Because the orbital angular momentum is zero in Gd^{3+}, the exchange integral becomes diagonal with respect to the azimuthal quantum number of 4f states, and to (Γ, γ). Thus the exchange interaction becomes isotropic with a factor

$$W_{\boldsymbol{k},\boldsymbol{p}} = \sum_{\Gamma\gamma} d^{(5d)}_{\Gamma\gamma}(\boldsymbol{k})^* d^{(5d)}_{\Gamma\gamma}(\boldsymbol{p}). \quad (3)$$

The RKKY interaction $I(\boldsymbol{q})$ is given by

$$I(\boldsymbol{q}) = \frac{2J^2}{N} \sum_{\boldsymbol{k}} |W_{\boldsymbol{k},\boldsymbol{k}+\boldsymbol{q}}|^2 \frac{f(\epsilon_{\boldsymbol{k}+\boldsymbol{q}}) - f(\epsilon_{\boldsymbol{k}})}{\epsilon_{\boldsymbol{k}} - \epsilon_{\boldsymbol{k}+\boldsymbol{q}}}$$

with $f(\epsilon)$ being the Fermi function. The intrapocket contribution to $I(\boldsymbol{q})$ comes from such $\boldsymbol{k}$ and $\boldsymbol{k}+\boldsymbol{q}$ that belong to the same pocket of the conduction band. In addition, there arises the interpocket contribution explained earlier. Let us take the free-electron-like dispersion and set $|W_{\boldsymbol{k},\boldsymbol{k}+\boldsymbol{q}}|^2$ constant in order to see the consequence of the interpocket contribution in the simplest manner.

In order to keep the lattice periodicity, we take summation over the reciprocal lattice vectors $\boldsymbol{G}$ rather than restricting the $\boldsymbol{k}$-summation within the Brillouin zone. The $\boldsymbol{G}$-summation corresponds to inclusion of higher energy bands. Namely we introduce

$$\tilde{\Pi}(\boldsymbol{q}) = \sum_{\boldsymbol{G}} F(\boldsymbol{q}+\boldsymbol{G})\Pi(\boldsymbol{q}+\boldsymbol{G}),$$

where $F(\boldsymbol{q}+\boldsymbol{G})$ is a form factor to be specified later, and $\Pi(\boldsymbol{q})$ is the Lindhard function multiplied by the partial density of states at the Fermi level. The Fermi wave number k_F is given by $k_F a/\pi = \pi^{-1/3} = 0.9656/\sqrt{2}$, which means that the three spherical Fermi surfaces barely touch with one another. In the real RB_6 system, the Fermi surface also contains a fine structure along $(1,1,0)$ and equivalent directions.[8,9)]

Adding both intrapocket and interpocket contributions we obtain for $\boldsymbol{q} \in$ Brillouin zone:

$$I(\boldsymbol{q}) = J^2[3\tilde{\Pi}(\boldsymbol{q}) + 2\sum_{i=1}^{3}\tilde{\Pi}(\boldsymbol{q}-\boldsymbol{K}_i)] \equiv J^2\chi(\boldsymbol{q}),$$

where $3\tilde{\Pi}(\boldsymbol{q})$ accounts for the three equivalent pockets, and $\tilde{\Pi}(\boldsymbol{q}-\boldsymbol{K}_i)$ describes the interpocket polarization. The $\boldsymbol{K}_i$'s are given by $\boldsymbol{K}_1 = (0,1/2,1/2), \boldsymbol{K}_2 = (1/2,0,1/2), \boldsymbol{K}_3 = (1/2,1/2,0)$ in units of $2\pi/a$. The factor 2 for the interpocket term enters because each pocket can be both starting and ending states of the transition. For simplicity we take the form factor such that $F(\boldsymbol{k}) = 1$ if $|k_\alpha| < 6\pi/a$ for all components $\alpha = x, y, z$ and zero otherwise. The choice of the cut-off in the form factor hardly influences the $\boldsymbol{q}$-dependence of the RKKY interaction, although it does influence the absolute value. Specifically with $F(\boldsymbol{q}+\boldsymbol{G}) = 1$ for all $\boldsymbol{G}$, $\tilde{\Pi}(\boldsymbol{q})$ diverges logarithmically by summation over $\boldsymbol{G}$.

Figure 1 shows $\chi(\boldsymbol{q})$ in the X-M-R plane of the Brillouin zone with $X = (0,0,1/2), M = (1/2,0,1/2)$ and $R = (1/2,1/2,1/2)$. The unit of ordinate is such that $\Pi(0) = 1$, and the large numerical value of $\chi(\boldsymbol{q})$ comes from summation over $\boldsymbol{G}$. For the intersite interaction, only the variation in the $\boldsymbol{q}$-space is relevant since the average of $\chi(\boldsymbol{q})$ represents the intra-site contribution.

We have also made a scan of $\chi(\boldsymbol{q})$ along $(1/4,1/4,q_z)$ and found that the peak indeed occurs at $q_z = 1/2$. It is apparent that the interaction favors the magnetic order near the center of the X-M-R plane, namely around $(1/4,1/4,1/2)$. Since the ridge extends more toward M rather than R, an incommensurate structure with $q_x \neq q_y$ can be realized by slight change of the system parameters.

We now analyze in more detail the character of the conduction band, which consists mainly of t_{2u} molecular orbitals of 2p electrons in B_6 clusters hybridized with e_g orbitals of 5d electrons. One of the t_{2u} orbitals has the angular dependence $z(x^2-y^2)$ if seen from the center of the B_6 cluster, and hybridizes best with the 5d x^2-y^2 orbital at neighboring rare-earth sites. Since $z(x^2-y^2)$ changes sign below and above the B_4 plane, the wave number $(0,0,1/2)$ gains the bonding energy optimally.[9)] Thus the bottom of the conduction band goes to X_z and

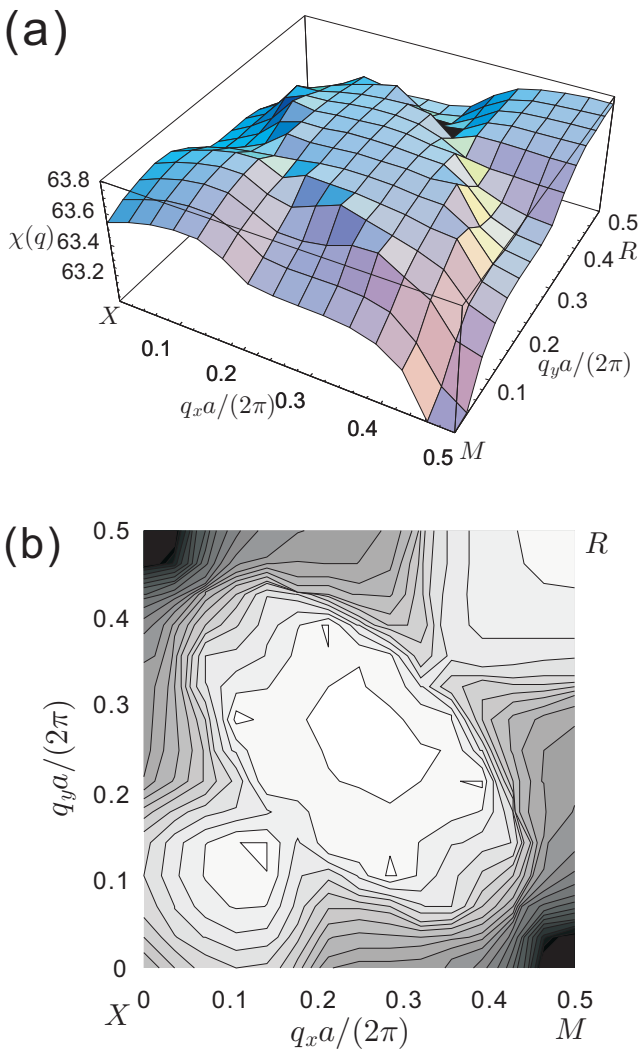

Fig. 1. Wave-number dependence of the intersite interaction in the X-M-R plane: (a) three-dimensional plot; (b) contour plot.

equivalent points. For $\Gamma = e_g$ we use a simplified notation $(\gamma|\boldsymbol{k}) = d^{(5d)}_{\Gamma\gamma}(\boldsymbol{k})$ with γ being either the state x^2-y^2 or $3z^2-r^2$. Then we have a large amplitude $(x^2-y^2|X_z)$, while $(3z^2-r^2|X_z)$ is negligible. At another point $X_x = (1/2,0,0)$, the wave function has the character of y^2-z^2 which can also be represented by

$$|y^2-z^2\rangle = -\frac{1}{2}|x^2-y^2\rangle - \frac{\sqrt{3}}{2}|3z^2-r^2\rangle, \qquad (4)$$

with use of the basis set at X_z. Thus the orbital flip from $|x^2-y^2\rangle$ to $|y^2-z^2\rangle$ can take place even with the cubic symmetry. We note that the finite overlap does not contradict with the orthogonality of Bloch functions with different $\boldsymbol{k}$.

The relative weight of the interpocket polarization against the intrapocket one should influence the detailed behavior of $I(\boldsymbol{q})$. We estimate from the above argument the weight factor $W_{\boldsymbol{k},\boldsymbol{p}}$ for $\boldsymbol{k} = X_z$ and $\boldsymbol{p} = X_x$ relative to $W_{\boldsymbol{k},\boldsymbol{k}}$ as

$$W_{\boldsymbol{k},\boldsymbol{p}}/W_{\boldsymbol{k},\boldsymbol{k}} \sim -1/2.$$

These points X_z and X_x, however, are not on the Fermi surface. In the region where two pieces of the Fermi sur-

face almost touch with each other, the interpocket contribution connecting the nearby $\boldsymbol{k}$ states should have a larger weight factor than the intrapocket one with remote $\boldsymbol{k}$ and $\boldsymbol{p}$. We have made a tight-binding calculation taking the e_g and t_{2u} orbitals, and examined the character of the wave functions at various points in the Brillouin zone. It is found that 2p-electron weight is larger than the 5d-electron weight in general, and the latter changes gradually from $|x^2-y^2\rangle$ to $|y^2-z^2\rangle$ as $\boldsymbol{k}$ moves from X_z to X_x. In a future work, we shall evaluate $W_{\boldsymbol{k},\boldsymbol{p}}$ by using realistic wave functions.

The presence of orbital degeneracy in rare-earth ions other than Gd makes it necessary to consider more complicated form of H_{df}. Namely not only the spin exchange interaction but multipole interactions also enter.[7,10,11] As long as the conduction band consists purely of e_g for the 5d electron part, the wave-number dependence of the multipole intersite interactions is the same as that of the exchange interaction. Actually, however, $t_{2g}(=\Gamma_5)$ also enters into eq.(2). In the presence of orbital degeneracy, $W_{\boldsymbol{k},\boldsymbol{p}}$ is no longer given by eq.(3) but with different weights for each Γ.[7] Moreover, hybridization between 4f electrons and boron 2p electrons may become important in the open-shell case. The hybridization constitutes another mechanism of the intersite interaction.

With these complications in mind we proceed to analysis of the exchange interaction in NdB_6 where the spin-wave spectrum has been measured. The dipole part of H_{df} can be taken in the same form as eq.(1) except that $\boldsymbol{S}_i$ is replaced by the angular momentum operator $\boldsymbol{J}_i$ with $J=9/2$. With only the magnetic intersite interaction, the easy axis of the magnetic moment should be along $(1,1,1)$.[12] Actually the moment is parallel or antiparallel to $(0,0,1)$, which has been explained in terms of ferroquadrupolar interaction.[13,14] With inclusion of the magnetic and Γ_3-type quadrupolar interactions, we consider the following model:

$$H=-\sum_{(i,j)} I_{ij}\boldsymbol{J}_i\cdot\boldsymbol{J}_j-g_3'\sum_i\left(\langle O_2^0\rangle O_{2i}^0+3\langle O_2^2\rangle O_{2i}^2\right),$$

where we assume that the average of the quadrupole moment does not depend on a site. Other interactions such as the Γ_5-type quadrupolar interaction[15] are neglected since they do not affect the spin-wave spectrum.

The CEF ground state is $\Gamma_8^{(2)}$, which is four-fold degenerate, and the first excited state lies 132∼135 K above.[13,16] We introduce the Pauli matrix $\sigma^\alpha(\alpha=x,y,z)$ to describe the Kramers pair, and another Pauli matrix τ^α to describe the orbital pair in the $\Gamma_8^{(2)}$ quartet. Then the angular momentum operator J^α within the $\Gamma_8^{(2)}$ subspace is written as

$$J^\alpha=\frac{1}{2}(\xi+\eta T^\alpha)\sigma^\alpha,$$

where $\xi=-0.883$ and $\eta=-4.712$ are numerical constants corresponding to the Lea-Leask-Wolf[17] parameter $x=-0.82$.[13] The orbital effect on the magnetic moment is described by T^α with $T^z=\tau^z$ and

$$T^{x,y}=-\tau^z/2\pm\sqrt{3}\tau^x/2.$$

In the Néel state the $\Gamma_8^{(2)}$ quartet undergoes a Zeeman splitting by the molecular field. This splitting induces a finite quadrupole moment which is enhanced by positive g_3'. Then the lowest level is characterized by $(\tau^z,\sigma^z)=(+,\uparrow)$ in the A-sublayer and $(+,\downarrow)$ in the B-sublayer. One may expect two branches corresponding to excitations

$$(+,\sigma)\rightarrow(\pm,-\sigma),$$

with intensities $I_\pm$. Here $\sigma=\uparrow,\downarrow$ in the A- and B-sublayers, respectively. The intensity ratio I_+/I_- is given by

$$I_+/I_-=(2\xi/\eta-1)^2/3\sim 0.13.$$

Thus we identify the observed branch as the inter-orbital transition $(+,\sigma)\rightarrow(-,-\sigma)$, and assume that intra-orbital branch was not detected because of the small intensity.

By neglecting the small matrix elements for intra-orbital magnetic excitations, we obtain a reduced model which keeps only the two levels leading to I_-. Assuming the A-type antiferromagnetic structure with $\boldsymbol{Q}=(0,0,1)$, we obtain the excitation spectrum by the standard spin-wave theory as

$$\omega_{\boldsymbol{q}}^2=[J(\boldsymbol{q})-\Delta][J(\boldsymbol{q}+\boldsymbol{Q})-\Delta], \tag{5}$$

where $J(\boldsymbol{q})$ is the Fourier transform of $J_{ij}=\left(3\eta^2/16\right)I_{ij}$, and

$$\Delta=\frac{8\xi(\xi+\eta)}{3\eta^2}J(\boldsymbol{Q})+\frac{9}{2}(\xi-\eta-9)^2g_3'. \tag{6}$$

The spectrum given by eq.(5) was also postulated in the previous work, where $\omega_{\boldsymbol{q}}$ experimentally measured was fitted by intersite interactions up to third neighbors. The authors of ref.6 noted that the calculated Néel temperature was about half of the experimental one, 8∼9 K. We point out further that the substantial softening around $(1/4,1/4,0)$ was not reproduced by the previous fit.

In view of the fact that the RKKY interaction has a long range, we have included a sufficient number (= 34) of intersite interactions J_{ij}. The comparison between theory and experiment is shown in Fig.2. The experimental spectrum is well reproduced by our fit. The fit gives $J(\boldsymbol{Q})=1.16$ meV and $\Delta=1.47$ meV. Then we obtain $g_3'=108$ mK from eq.(6). This value is in excellent agreement with experimental one, $g_3'\sim$100 mK, deduced from elastic constant.[13] In the mean-field approximation the Néel temperature is not influenced by g_3', and is given by

$$T_{\rm N}^{\rm MF}=\frac{4}{3}\frac{\xi^2+\eta^2}{\eta^2}J(\boldsymbol{Q}),$$

which is 9.3 K with the fitted value of $J(\boldsymbol{Q})$.

Figure 3 shows $J(\boldsymbol{q})$ in the X-M-R plane. The maximum of $J(\boldsymbol{q})$ occurs at $(0,0,1/2)$ in consistency with the A-type order. In addition, there appears a local maximum near $(1/4,1/4,1/2)$. The latter indicates a tendency toward the ordering with $\boldsymbol{q}=(1/4,1/4,1/2)$, and brings about the softening of $\omega_{\boldsymbol{q}}$ near this wave number. We note that the overall behavior of $J(\boldsymbol{q})$, and thus

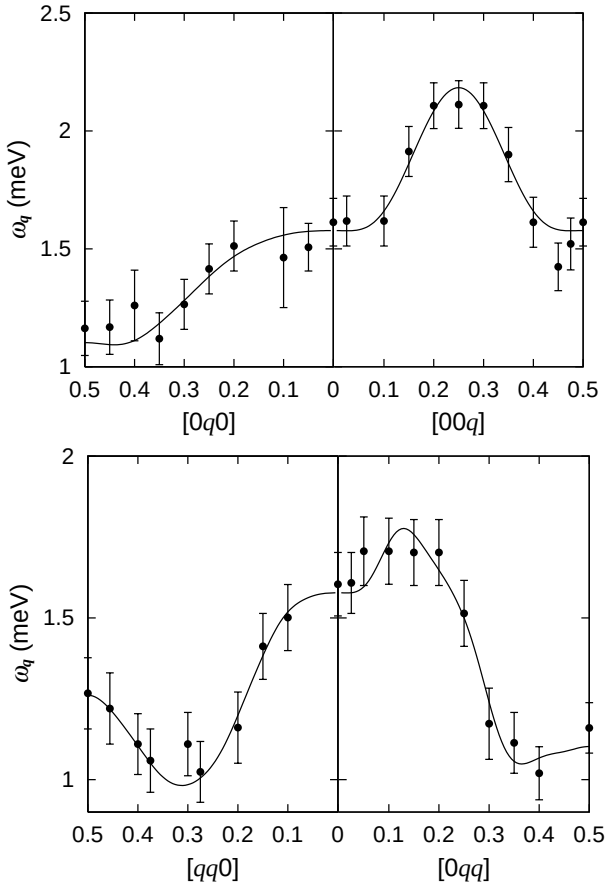

Fig. 2. The magnetic excitation spectrum in NdB_6 along various symmetry directions. Experimental data[6] are shown by solid circles with error bars, and the solid lines are theoretical fits.

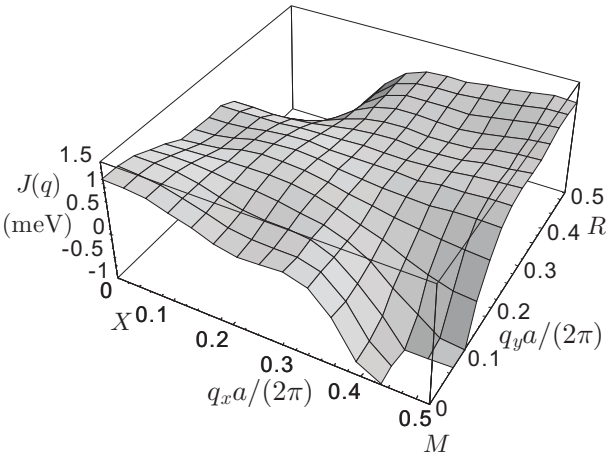

Fig. 3. Wave-number dependence of $J(\boldsymbol{q})$ in the X-M-R plane.

$I(\boldsymbol{q}) = (16/3\eta)^2 J(\boldsymbol{q})$, is similar to the result of the interpocket polarization model shown in Fig.1. This similarity supports relevance of the model to real RB_6 systems. The difference should mainly come from our simplification for $W_{\boldsymbol{k},\boldsymbol{p}}$ and $\epsilon_{\boldsymbol{k}}$, and partly from the presence of orbital degeneracy, hybridization, and correlation effect among conduction electrons.

In this paper we have concentrated on the $\boldsymbol{q}$-dependence of the intersite interaction $I(\boldsymbol{q})$. As the magnetization grows, the associated nonlinearity favors a commensurate structure in general. Then the maximum of $I(\boldsymbol{q})$ does not necessarily give the ordering wave number at the ground state. We suggest that the incommensurate-commensurate transition in PrB_6 may be interpreted along this line. It should be worth investigating detailed features which depend on 4f-electron configurations of each rare-earth species.

Another feature to be addressed with finite order parameters is the direction of magnetic moment at each site. Even with the same $\boldsymbol{q} = (1/4, 1/4, 1/2)$, the moment patterns are rather different between CeB_6[1] and DyB_6.[18] While in CeB_6 the nearest-neighbor moments are orthogonal to each other and within the (001) plane, the moments in DyB_6 point to $(1/2, 1/2, 1/2)$. The latter is consistent with the magnetic anisotropy in the paramagnetic region. In this connection it is interesting to inquire into the spin patterns of GdB_6 at low temperature, since the magnetic anisotropy in the paramagnetic region is extremely small.[19]

Acknowledgements

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